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ADSORPTION MOBILITY AND ORGANIZATION OF ORGANIC
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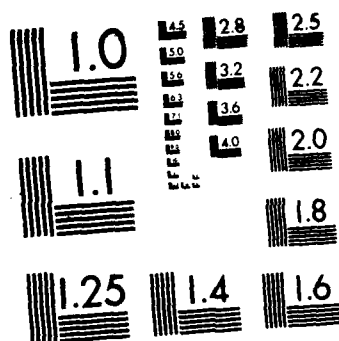
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ADSORPTION, MOBILITY AND ORGANIZATION OF ORGANIC MOLECULES AT CLAY
SURFACES PROBED BY PHOTOPHYSICS AND PHOTOCHEMISTRY

THIRD INTERIM REPORT

10/12/87

UNITED STATES ARMY
EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY
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1. INTRODUCTION

In a previous study was noticed that organic, detergent like molecules, adsorbed on a clay surface form clusters (1). This aggregation is caused by hydrophobic interactions between the adsorbed molecules (2). To obtain more information about this cluster formation a spectroscopic study is performed on clay suspensions with varying loadings of probe and detergent.

Also, different clays are used in order to find out the influence of the different aggregation properties of the clay particles in aqueous suspensions.

In addition to the detergents studied until now, one and two tailed ammonium surfactants, a previously developed detergent methacryloyloxy-ethylmethyldiodecylammonium chloride with a polymerisable headgroup is studied. The purpose is to study the polymerization of ^{the} this detergent on a clay surface, and to study the properties of clay particles coated with the obtained polymer. Such ionic polymers are used in a variety of industrial products as thickeners, dispersants, flocculants, ion exchange resins, etc... Their suitability for these applications can be referred to the great hydrophilicity and especially to the highly polar character which enable these substances to adsorb other polar compounds, such as dye-stuffes, charged colloidal particles and ions.

Before proceeding with this polymerization however, the properties of the monomer adsorption have been studied first. As fluorescent probe, 3-(1-pyrenyl)propyltrimethylammonium bromide (P3N) has been used (1). Three different clays are used in our study : Barasym, a synthetic mont-morrillonite, Hectorite and Laponite, a synthetic Hectorite.

2. EXPERIMENTAL RESULTS

2.A. Synthesis of methacryloyloxyethylmethyl didocylammoniumchloride

The synthesis of this monomer was repeated on the basis of a synthetic scheme worked out in a previously submitted report.

2.B. Discontinuity at low loadings of P3N

2.B.1. Absorption spectra

The absorption spectra of a series of loadings of P3N, adsorbed on Laponite, are investigated. This experiment has been performed by keeping the probe concentration constant and varying the clay concentration.

In an aqueous solution, the maximum of the 11a absorption band of P3N is situated at 343 nm. After adsorption on the clay surface however, this maximum shifts to 347 nm. This shift is observed for all the different loadings. The 11b absorption band shows only a minor shift.

In figure 1, the absorbance is depicted as a function of the loading. It can be seen that this absorbance, after remaining constant at lower loadings decreases with increasing loading.

Furthermore, a modification of the vibrational fine structure of the absorption spectra of P3N is observed at higher loadings, as can be seen in figure 2. All these observations indicate ground state interactions between the adsorbed probes, at least of loadings above 2.5% of the C.E.C.

The fact that in the absorption spectra no maximum at 343 is observed indicates the presence of ground state association, already at low loadings.

2.B.2. Emission spectra

In figure 3, fluorescence spectra of P3N adsorbed on Laponite a loading of 0.76% is given. Even at this low loading a large amount of excimer emission is observed. Excitation spectra taken in the monomer and excimer region indicate a formation of excimers by the ground state aggregates and not by the monomers. The excitation spectra in the monomer region shows a normal pyrene absorption spectrum with a maximum at 343 nm. This means that at low loadings some monomers are present on the clay surface, but the concentration is low, since in absorption spectra the monomer is not observed.

In figure 4 the IE/IM ratio is plotted as a function of the loading.

In the first part of figure 4, at low loadings, the ratio remains constant. This suggests that the distribution of the molecules on the surface does not alter at those low loadings. At a loading of $\pm 15\%$ a steep decrease is observed. This indicates a sudden modification of the distribution and/or orientation of the adsorbed molecules on the surface. Work is in progress to elucidate this phenomenon.

At high loadings, over 70% coverage, a decrease is observed. This is probably due to the fact that the clay surface is in competition with the solvent.

2.C. Time dependence of the distribution at low loadings in presence and absence of detergent

Such a study has until now only been executed with Laponite suspensions, but will in a later stage be extended to the other two clays. It has been noticed that the absorbance of P3N adsorbed in Laponite decreases with time. As a consequence, the fluorescence characteristics also change (figure 5). This change however seems to be dependent on the loading and/or the concentrations of the clay.

Viscosity and light scatter experiments (3) show an increase in particle size of the clay suspensions as a function of time. It seems that with time, the clay particles aggregate. This aggregation induces changes in ground and excited state properties of the adsorbed molecules.

These aggregation phenomena can thus be followed by absorption and fluorescence measurements.

The time dependence is also influenced by the loading of adsorbed molecules. At higher loadings, the aggregation occurs more rapidly. The aggregation seems to be enhanced by adsorbing detergent like molecules. Probably, the detergent like molecules tend to come together due to hydrophobic interactions. These interactions induce an aggregation of the clay platelets.

2.D. Influence of the type of clay on the spectroscopic properties at low loadings

Three different clays are used, to study the influence of the type clay on the spectroscopic properties of adsorbed molecules : Hectorite, Laponite and Barasym. The most important difference between these three clays is their behaviour in an aqueous suspension. Barasym forms large particles, containing a number of individual platelets. Adsorption only occurs on the external surface of these large particles. The molecules can not penetrate between the individual clay platelets. Hectorite also forms rather large particles but by a swelling mechanism, the molecules can adsorb on the interlamellar surface. Laponite, at a moderate ionic strength, forms a suspension of individual platelets.

Molecules adsorbed on Laponite and Barasym show an excimer emission with a maximum at 480 nm, while those adsorbed on Hectorite show a maximum at 475 nm. The difference between Laponite and Barasym on the one hand and Hectorite on the other is the availability of the interlamellar surface for Hectorite. These observations indicate a difference in excimer

geometry of the excimers formed at the external and interlamellar surface.

Another difference between the two types of clays are the excitation spectra. For Laponite and Barasym, there is a substantial difference between the excitation spectra taken at 378 and 480 nm. This can be explained by assuming that the fluorescence at 378 comes essentially from P3N adsorbed on the surface as monomers and that the one at 480 nm is due to excimer formation from aggregated P3N molecules. A Hectorite suspension however, does not show those two different excitation spectra. In both regions, a shifted excitation spectra is obtained. This indicates the absence of a substantial amount of monomers on Hectorite. It seems that P3N is only adsorbed as a monomer on the external surface of a clay particle. The amount of external surface for Hectorite is much smaller than for Laponite and Barasym, resulting in the absence of a monomer excitation spectrum.

3. REFERENCES

1. K. Viaene, J. Caigui, R.A. Schoonheydt, F.C. De Schryver, *Langmuir* 1987, 3, 107
2. K. Viaene, M. Crutzen, B. Kuyima, R.A. Schoonheydt, F.C. De Schryver, to be published
3. M. Crutzen, Doctoral Thesis

Fig. I

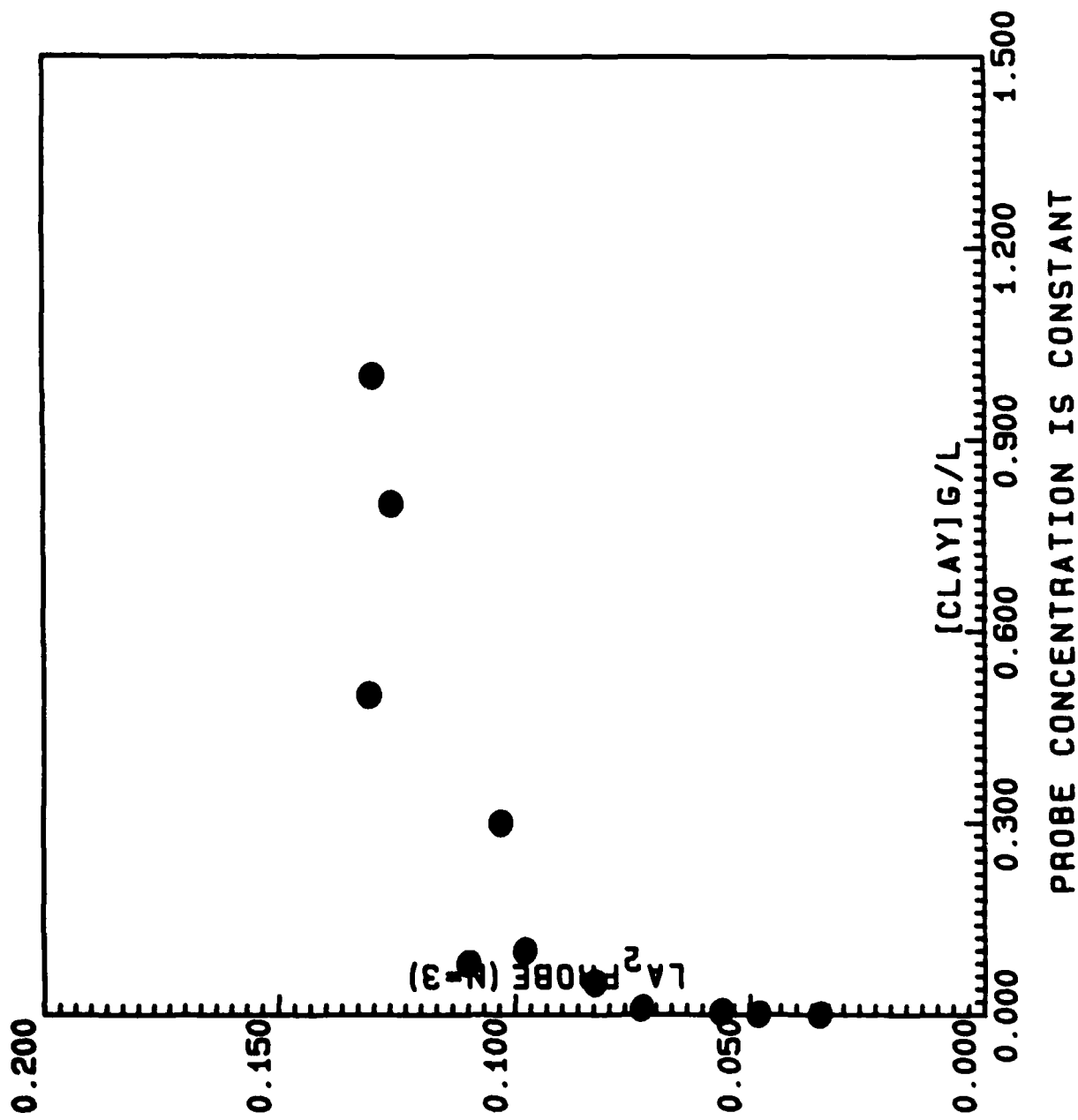


Fig. II a

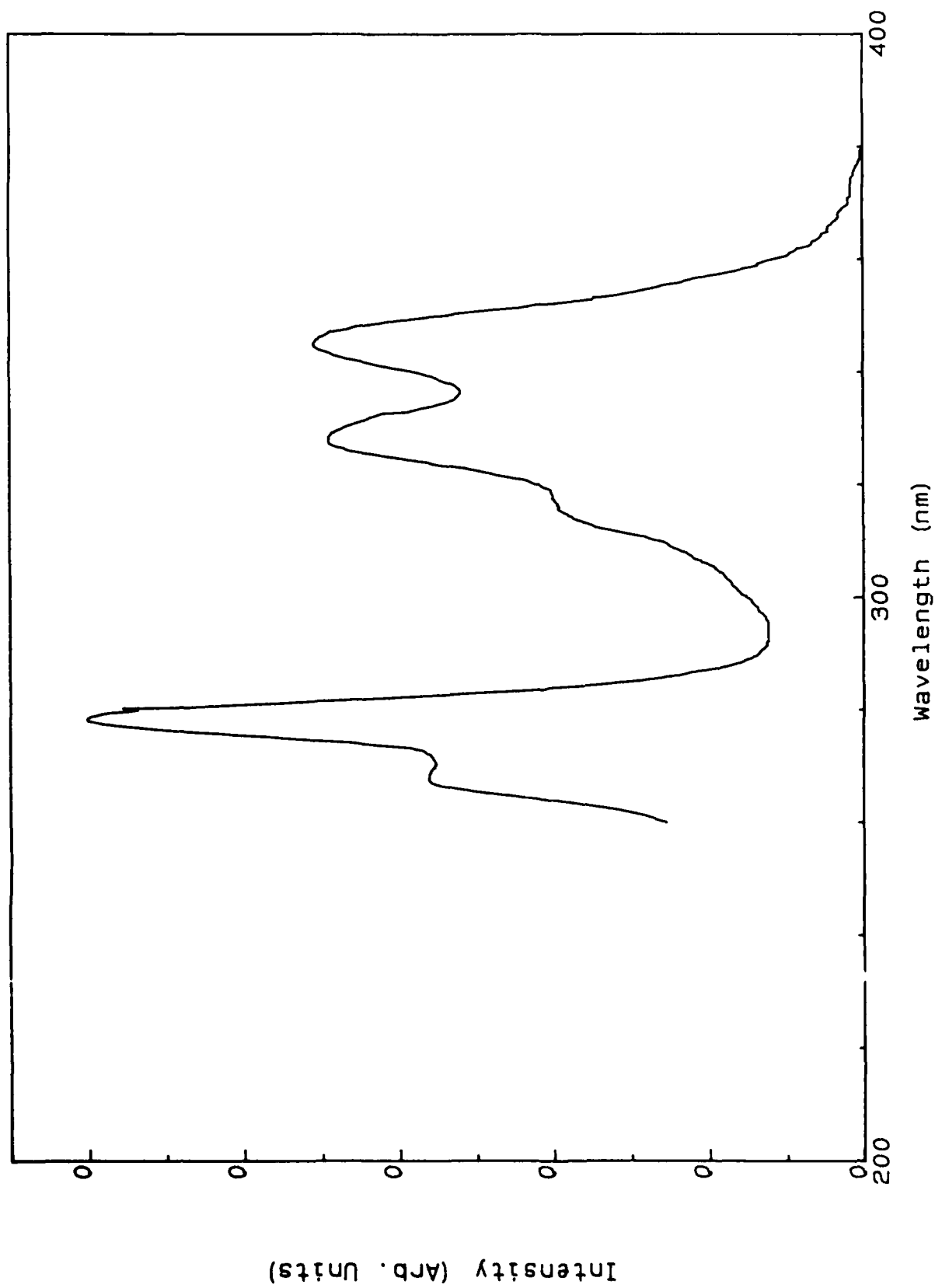


Fig II 6

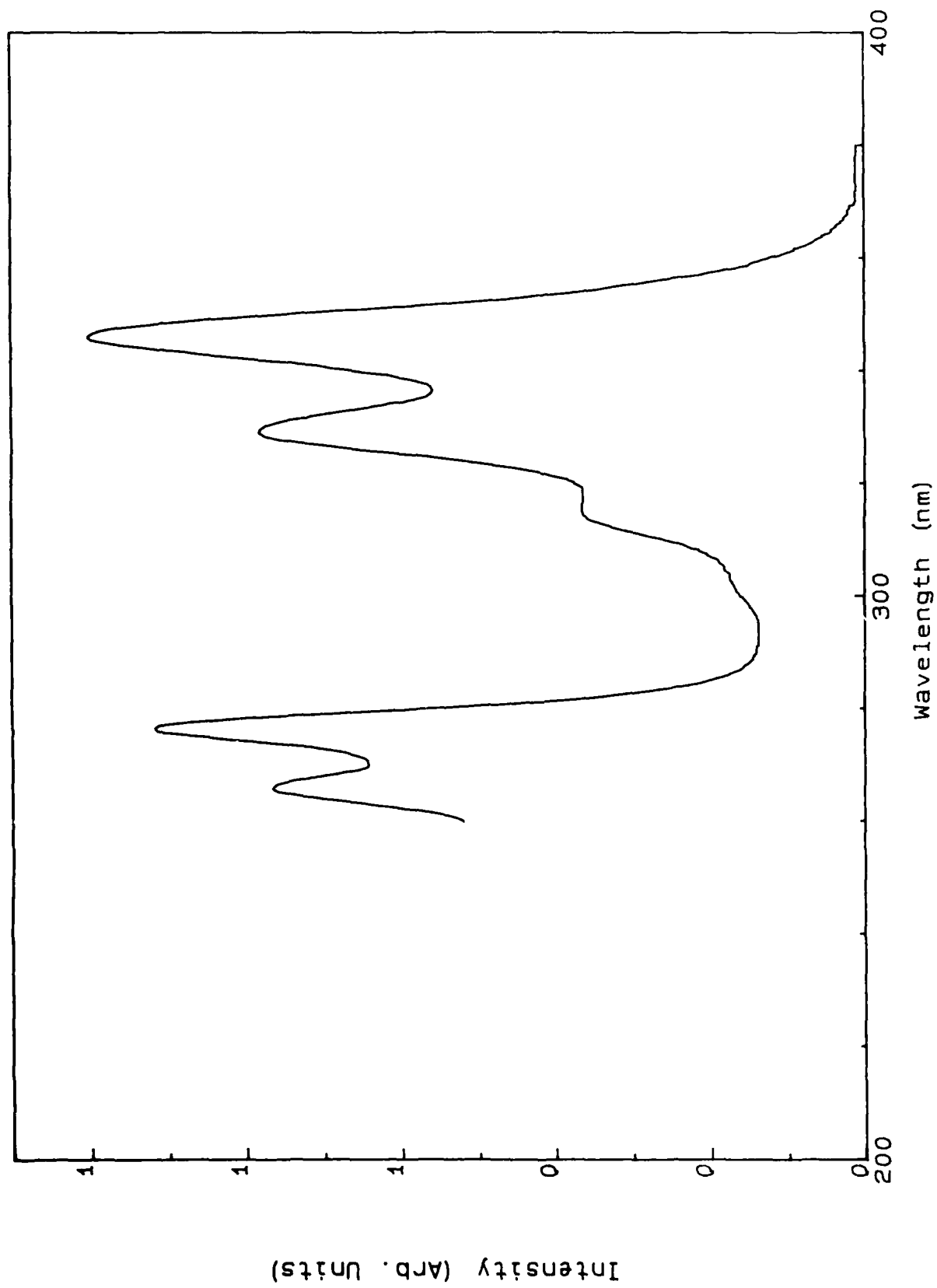


Fig. III

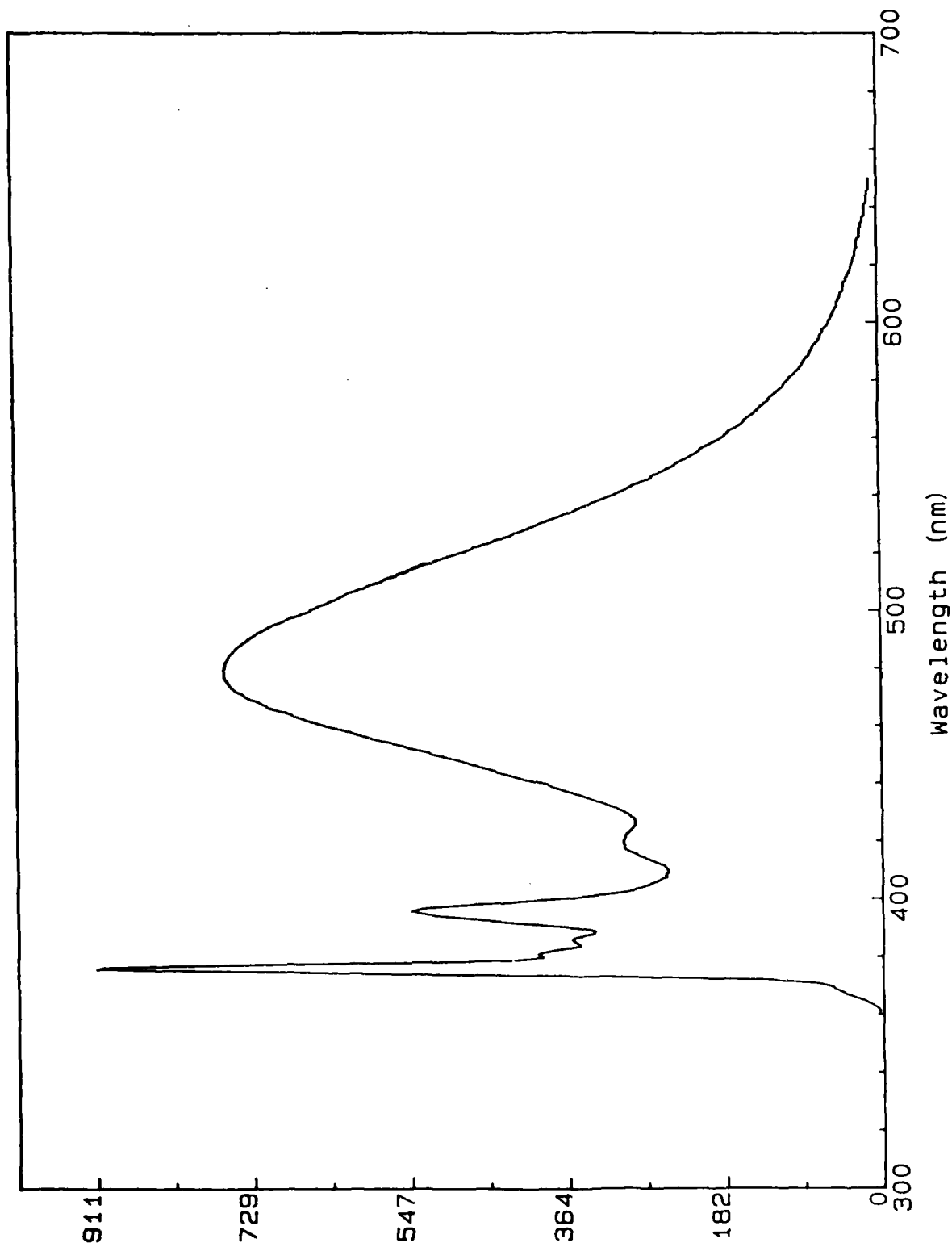
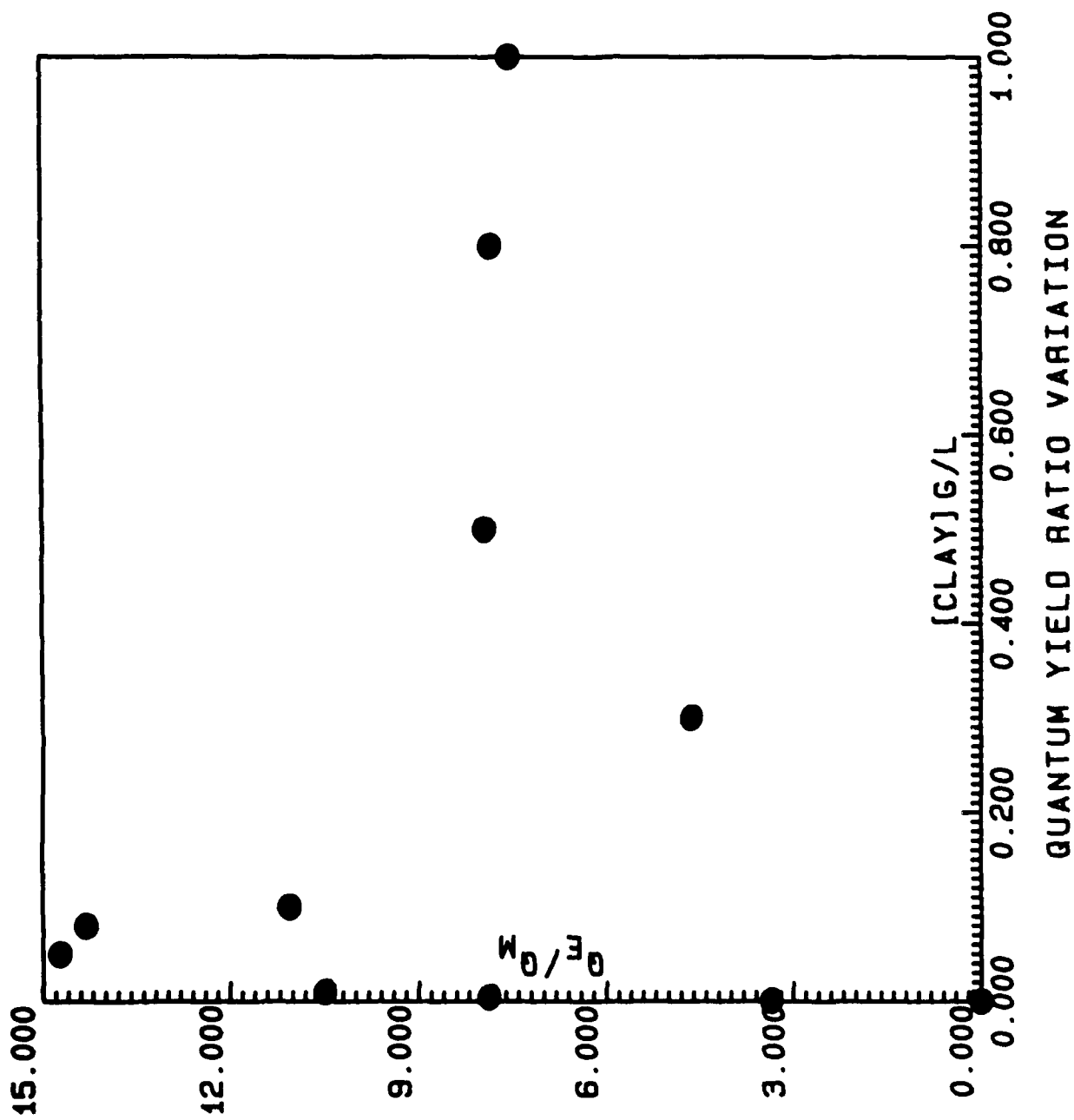


FIG. IV



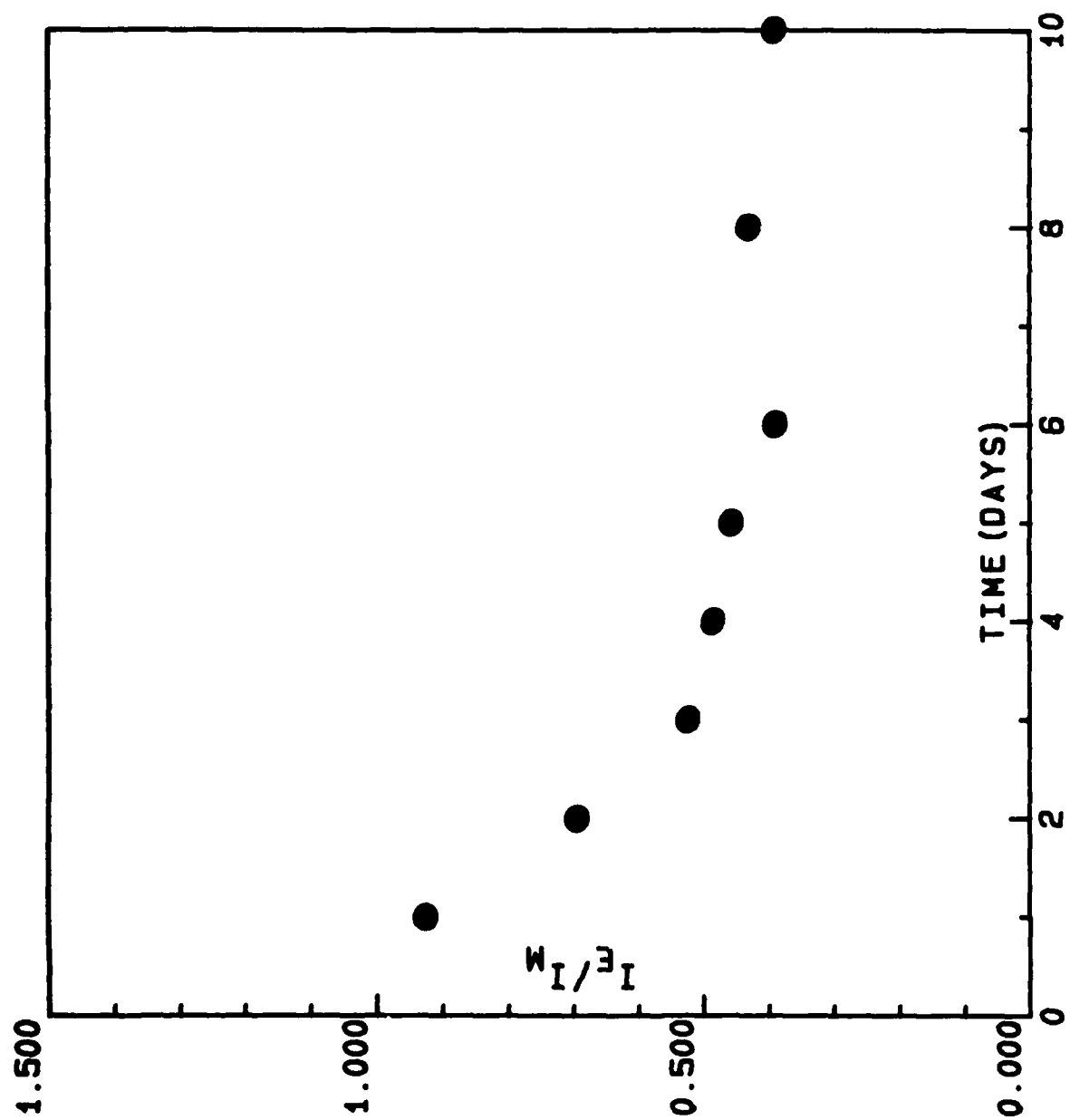


Fig. 24

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